

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
3 July 2003 (03.07.2003)

PCT

(10) International Publication Number  
**WO 03/053149 A1**

(51) International Patent Classification<sup>7</sup>: **A23D 7/00, 7/04, A23L 1/035, 1/0522, A23P 1/06, 1/02**

(21) International Application Number: **PCT/EP02/13310**

(22) International Filing Date:  
27 November 2002 (27.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
01310850.1 21 December 2001 (21.12.2001) EP

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER N.V.** [NL/NL]; UNILEVER N.V., Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London, Greater London EC4 4BQ (GB).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai\_400 020 (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **FARRER, Donald** [GB/GB]; 38 Paddocks Road, Rushden, Northamptonshire NN10 6RY (GB). **FINLAYSON, Roger, Morley** [ZA/NL]; Unilever R & D Vlaardingen, Olivier van

Noortlaan 120, NL-3133 AT Vlaardingen (NL). **FOSTER, Timothy, John** [GB/GB]; Unilever R & D Colworth, Colworth House, Sharnbrook, Bedfordshire MK44 1LQ (GB). **PELAN, Edward, G** [GB/NL]; Unilever R & D Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). **RUSSELL, Alison, Louise** [GB/GB]; Unilever R & D Colworth, Colworth House, Sharnbrook, Bedfordshire MK44 1LQ (GB). **THOMAS, Anna** [NL/NL]; Unilever R & D Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(74) Agent: **WALLACE, Sheila, J.**; Lloyd Wise, Commonwealth House, 1-19 New Oxford Street, London WC1A 1LW (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **INSTANT EMULSION**

(57) Abstract: A base composition is provided which is suitable for the preparation of a spreadable emulsion with multiple functionality. The base composition is turned into a spreadable emulsion by a consumer. The preparation of the spreadable emulsion is accompanied by a change in sensory properties.



**WO 03/053149 A1**

Instant emulsion

### **Field of the invention**

The invention relates to a method for the preparation of a spreadable oil and water containing emulsion and to a base composition suitable for preparation of this spreadable oil and water containing emulsion.

### **Background to the invention**

Kitchen products that are suitable for use in frying, baking, and spreading (on bread, toast or the like) are well known for decades. These products are generally offered to a consumer in the form of a final product in a tub or wrapper.

Such products have the disadvantage that they have a limited storage stability, especially leading to products with phase separation upon storage at a temperature of about room temperature (20 to 35 °C). In US-A-4160850, this disadvantage is acknowledged. Hence this document provides a shelf-stable mix suitable for consumer preparation of a spreadable butter substitute. However, the products provided therein require a set of actions which take a long time, require the use of relatively sophisticated electrical equipment and in many cases recommend storage of the product in a refrigerator to completely stabilize the emulsion.

Furthermore these products are generally considered as standard products which use is generally automatic without recognition of any specific feelings upon its use. These products are however used daily in many households and could provide variation and excitement in their use provided they are delivered in the appropriate format.

The use of concentrates and powders for preparing an emulsion is already known for dressings, beverages and similar products. EP-A-796567 discloses a process for the preparation of a free-flowing and instantly soluble granular food product. Granules are dissolved or dispersed in warm or boiling water to obtain a final emulsion product.

However none of the documents relating to instant preparation of dressings or beverages teaches how traditional, spreadable products may be prepared or whether the technology is applicable for such products as well. It is believed that in the current consumer society the simple provision of granulates or a concentrate will not be sufficient to catch the consumer's interest in a product and therefor one of the aims was to provide a process and product which do attract the consumer's attention and lead to multiple and consistent purchasing over a long period of time.

It is an object of the invention to provide an attractive process for the preparation of a spreadable oil and water containing emulsion and a base composition suitable for use in this process.

Another object is to provide a base composition for preparing the above kitchen products which are easy and interesting to prepare and attractive for a consumer to purchase. Preferably this base composition is easy to make and creates curiosity and interest from a consumer.

30

#### Summary of the invention

It has surprisingly been found that at least part of the objectives are met by a process which is characterised by a surprising effect, whereby a base composition is provided that can be formed into an emulsion by manual operation within a short time while showing a perceivable change in at least one sensoric property.

Therefore the invention relates to a method for the preparation of a spreadable oil and water comprising emulsion, comprising mixing a base composition with oil and/or water by a simple, preferably manual, operation, wherein the spreadable emulsion is prepared within 3 minutes and the preparation is accompanied by a change in sensory properties which is demonstrated by an R-index in the R-index sensitivity test of more than 80%.

15

In a further aspect the invention relates to a base composition suitable for use in this process.

#### Detailed description of the invention

20

All percentages herein are by weight, calculated on total product, unless specifically indicated other wise.

The terms oil and fat are used interchangeably in this specification and claims.

25

For the purpose of this invention a base composition is defined as a product from which an emulsion comprising water and oil can be prepared. A base composition is for example referred to in US-A-4,160,850 wherein it is called a "shelf stable mix".

30

A base composition is also disclosed in not pre-published application WO-A-02/00030. In the art, base compositions are also referred to as instant products. Examples of instant

products are powders from which a salad dressing can be prepared by addition of water and/or oil.

For the purpose of the invention the term transparent also  
5 includes translucent embodiments.

The base composition according to the invention can be turned into a spreadable emulsion by the addition of at least water and/or oil and optionally other ingredients. Suitable sources  
10 for water include but are not limited to milk, (fruit) juice, tea, coffee and the like. Suitable sources for oil include but are not limited to the oils that are usually present in a consumer household such as olive oil, sunflower oil.

15 The base composition is suitable for preparing an edible emulsion. Edible means that the product is suitable for human consumption.

The emulsion resulting from the process according to the  
20 invention preferably has multiple functionality in spreading, baking, topping and frying.

The emulsion prepared from the base composition is spreadable. In the context of the invention, spreadable is defined by a  
25 combination of  $G'$  and Stevens value wherein the Stevens value, determined by the method illustrated in the examples, is preferably at least 50 g at 5 °C, more preferred from 50 to 800 g at 5 °C and  $G'$ , determined by the method illustrated in the examples, preferably ranges from 300 to 5000 Pa at 5 °C under  
30 the measuring conditions specified in the examples.

More preferred the Stevens value at 5 °C is from 50 to 500 g when measured with a so called mayonnaise grid to a penetration depth of 20 mm or, for harder products of from 100 to 500 g

when measured to a penetration depth of 10 mm with a cylindrical stainless steel probe of 7mm diameter.

Examples of known spreadable products include fresh cheese and dairy based spreads. Water continuous spreadable products are often milk based and optionally acidified as disclosed for example in WO-A-97/04660, DE-A-37101052, DE-A-3822082, EP-A-938,848 and EP-A-603,890.

Desirably, acceptable spreadable products show a tan delta value from 0.05 to 0.7 at a temperature of 20°C in combination with a strain (critical strain to failure) at tan delta  $d=1$  of from 0.6 to 2.20 determined by the method according to the examples.

It has surprisingly been found that the essential feature for instant products is that they are easy to prepare, in combination with a perceivable change in sensory properties obtained during the preparation process. We have found that consumers are attracted to those products that show this combination of characteristics whereas conventional instant products are dismissed as unattractive due to their dull image and complicated preparation. Especially consumers with relatively low income are adverse to obtaining instant products which require electrical apparatus such as a household mixer or a refrigerator for their conversion to the final product, simply because they often lack this equipment in their household.

Furthermore we have found that the change in sensory properties conjures surprise both during preparation and in respect of the final emulsion formed.

Therefore in the process according to the current invention, the base composition according to the invention can be converted to an emulsion by simple, preferably manual operation such as kneading, or mixing with a fork.

5

The base composition is converted into a final emulsion within 3 minutes. It is essential for a consumer that the time for preparation is at most three minutes, preferably at most 2 minutes, more preferred from 10 seconds to 1.5 minutes.

- 10 Consumers were found to reject products that take longer in their preparation and especially those which need refrigeration before they are ready for use.

The preparation of the emulsion is accompanied by a change in  
15 sensory properties. Sensory properties are for example flavour, texture, colour, aroma. These sensoric features can be perceived by a consumer when looking at, smelling or eating the product.

- 20 For the purpose of the invention texture is defined by many aspects of which the most common are listed below.

Viscosity as measured by the RVA-method disclosed in the examples is a measure for texture.

- 25 In a preferred embodiment the change in sensory properties is a change in this viscosity from about 0 to at least 1500 cP, preferably from 0 to about 1500 to about 12500 cP. The final product may harden further upon storage at a temperature below 10 °C.

30

Another aspect of texture is yield stress. Yield stress ( $G'$ ) is defined as the force required to deform a product. The method to determine  $G'$  is disclosed in the examples.

Preferably  $G'$  of the final product, determined by the method  
5 illustrated in the examples, ranges from 300 to 5000 Pa at 5 °C under the measuring conditions specified in the examples.

A change in colour is for example accomplished when a product turns from one distinct colour such as yellow to another such  
10 as white, or when two colours such as blue and yellow when combined are forming their mixing colour green.

The change from an at least partially transparent or translucent composition to an opaque composition is also encompassed within the definition of a colour change.

15 This can for example be obtained if the base composition is an at least partially transparent oil or water based composition to which a consumer adds the other component of oil or water thus forming an opaque emulsion upon mixing.

The change in colour can be determined by measuring absorption  
20 spectra, especially at a specific wave length.

It is essential for the claimed products that the change in sensory perception is perceived by the consumer. Preferably the change is such that the consumer is surprised that this effect  
25 is accomplished. Without wishing to be bound by any theory it is believed that the fact that the base composition is such that the consumer is able to create the final emulsion by simple operation while having the personal ability to create the change in sensory properties, is responsible for the high  
30 scores of these products in consumer tests. Contrary to the preparation of products such as soup from instant soup or dressings from a powder, the current final product is not simply a dilution or dissolving of subject matter to come to a



final product, but starting from a base composition from which by simple measures, a product is obtained which is generally perceived as including complex technology, namely margarine type products.

5

The change in sensory properties should be perceived by a consumer. It is generally known that each consumer may have a different sensitivity to product differences such as differences in texture, taste, colour and flavour. The level of change that is perceived by consumers is suitably defined by use of the R-index sensitivity test. The R-index sensitivity test is an alternative to the well known duo trio test and the triangle test. The R-index sensitivity test provides information whether products are significantly different and on the perceived size of the difference.

In the R-index test a reference product is compared to a series of products with different sensory properties and a person is asked to indicate whether the sample tested, compared to the reference product is:

- 20 - different, I am sure of it  
- different, I am not so sure of it  
- the same, I am not so sure of it  
- the same, I am sure of it

In the sample testing a reference product is included to serve as a control for the responses of the individual consumer. One test can compare 2 or more products to a reference.

The outcome is put into a response matrix according to table 1. From these data the R-index is calculated according to the calculation below.

30  
Table 1

|                              | Different<br>Sure | Different<br>Not sure | Same<br>not sure | Same<br>Sure |                |
|------------------------------|-------------------|-----------------------|------------------|--------------|----------------|
| Prototype<br>(vs. reference) | a                 | b                     | c                | d            | Np (= a+b+c+d) |
| Reference<br>(vs. reference) | e                 | f                     | g                | h            | Ns (= e+f+g+h) |

Calculation:

$$R\text{-index} = \frac{a(f+g+h)+b(g+h) + ch + \frac{1}{2}(ae+bf+cg+dh)}{NpNs}$$

The R-index represents the percentage of people that could detect a difference between two products. The higher the R-index, the more perceivable the change is. Tables are available  
5 in literature which indicate the level above which the R-index indicates a significant difference (depending on the sample size/number of tastings).

The applicable tables are disclosed in Bi, J. and O'Mahony, M., Table for testing the significance of the R-index. Journal of  
10 sensory studies 10 (1995) P341-347.

These tables give the minimum value of the R-index to be significant. Products for which the R-index is below this value are perceived as the same. The R-index sensitivity test is also disclosed by M. O'Mahony, J. Sensory Studies 7, (1992) 1-47.

15

For the current invention, the change in sensory properties should be such that the R-index in the R-index sensitivity test is more than 80%. Preferably the change in sensory properties is demonstrated by an R-index of more than 90%.

20

The emulsion prepared from the base composition according to the present invention may be suitable for a variety of applications, including preferably at least two of spreading (on bread or toast), baking, frying and topping. These uses are  
25 all encountered for traditional margarines and butter. The

multifunctional usage of the products adds to the attractiveness of the products for a consumer and also is believed to add to the surprising effect that the consumer herself prepares these products by simple manual operation.

5

It will be appreciated that a variety of base compositions may fulfil the requirements of the invention.

Below the preferred characteristics of the base composition are described.

10

The base composition is suitable for preparation of oil and water containing emulsions. According to a most preferred embodiment the base composition is suitable for the preparation of an oil in water emulsion.

15 In the context of the invention, the term suitable for preparation of an oil and water comprising emulsion, means that the base composition comprises at least part of the ingredients required to make a spreadable emulsion. Upon mixing this base composition with oil and/or water, and optionally further  
20 ingredients to make a final emulsion, the base composition is turned into an emulsion. Information on use and instructions regarding the addition of further ingredients may be provided orally but is preferably written information. Such written information is typically present on the packaging material of  
25 the base composition but may also be present as a loose leaflet or information brochure. Such information may consist of pictures or symbols rather than words.

The base composition is suitable for preparing a final emulsion  
30 within 3 minutes. This means that the base composition comprises ingredients such that this can be accomplished. Preferably the base composition is based on oil or fat.

Suitable fats or fat blends are preferably selected from the group comprising sunflower oil, soybean oil, rapeseed oil, cottonseed oil, olive oil, corn oil, groundnut oil, or low melting butterfat fractions and/or combinations thereof. These 5 fats may be partially hydrogenated or could f.e. be inter-esterified mixtures of hardened fats with liquid oils.

Preferably the base composition comprises an emulsifier selected from the group comprising lecithins, polyglycerol 10 polyricinoleate, monoglycerides, distilled monoglycerides, citric acid esters of monoglycerides, di-acetyl acetic acid esters of monoglycerides, lactic acid esters of monoglyceride, diglycerides, polyglycerol esters of fatty acids or sorbitan esters of fatty acids and polyoxyethylene compositions such as 15 sorbitan monopolyoxyethylene (Tween).

For the embodiment where a final emulsion which is fat continuous is prepared, polyglycerol polyricinoleate is the preferred emulsifier optionally in combination with other emulsifiers.

20 For the embodiment wherein a final emulsion which is water continuous is prepared, lecithins are the preferred emulsifiers, optionally in combination with other emulsifiers.

It will be appreciated that the ingredient composition of the 25 base composition is dependent on the fact whether it is water continuous or fat continuous. If the base composition is essentially based on fat or oil the inclusion of monoglycerides in the base composition is preferably avoided.

For example if the base composition is water continuous a 30 monoglyceride may be included as emulsifier.

Optionally the base composition further comprises a cold hydrating viscosifying ingredient. These ingredients are defined as those ingredients which will hydrate when added to water which is at a temperature of at most 60°C. The hydration  
5 leads to an increase of viscosity of the water in which the ingredient is dispersed. A test to determine suitable cold hydrating viscosifying (CHV) ingredients or systems is described in the examples. This test is further referred to as "RVA method".

- 10 Those agents or combinations thereof that show a final viscosity after 500 seconds of more than 1700 cP, or that show a final viscosity of from 300 to 600 cP in combination with a rate of hydration defined by the difference of viscosity between time is 0 seconds and time is 100 seconds of more than  
15 1200 cP/minute, are considered suitable cold hydrating viscosifying agents.

Suitable agents can also be found by microscopic examination of water swollen compositions. Suitable compositions for spread-like textures show intact, swollen particles, whereas ones  
20 showing irregular, "broken" structures tend to be less suitable.

Compositions that are intended for preparation of a final emulsion that is spreadable preferably comprise a cold  
25 hydrating viscosifying agent that gives a final viscosity of at least 1700 cP, preferably 1700 to 4000 cP in combination with a rate of hydration of at least 600, preferably 600 to 4000 cP/minute determined by the RVA- method according to the examples.

30

Preferably the cold hydrating viscosifying agent is selected from the group comprising cold swelling starch, inulin and gums which give final viscosities greater than 400cP with hydration

rates greater than 1500cP/min in the RVA method, or combinations thereof.

Especially preferred cold hydrating viscosifying agents are the so called "modified waxy maize starches".

The following guidelines provide guidance for selection of the cold hydrating viscosifying agent.

For the preparation of spreadable final oil in water emulsions, the use of a cold swelling starch as cold hydrating viscosifying agent is highly preferred. Suitable cold swelling starches are preferably selected from the group comprising Passelli EZ 1911<sup>tm</sup>, Ultratex A<sup>tm</sup>, Ultratex 1<sup>tm</sup>, Ultratex 2<sup>tm</sup>, Ultratex 2000<sup>tm</sup>, Ultratex 3<sup>tm</sup>, Ultratex 4<sup>tm</sup>, Instant Clearjel<sup>tm</sup>, Ultrasperse M<sup>tm</sup>, Ultrasperse 5<sup>tm</sup>, and Ultrasperse A<sup>tm</sup> and combinations thereof. The mentioned examples are available from National Starch.

Remyline AP<sup>tm</sup> ex Remy Industries is another suitable cold swelling starch.

Modified potato starch such as Paselli SA 2<sup>tm</sup> from Avebe was found to be less preferred for use as a cold hydrating viscosifying agent for preparation of final emulsions that are spreadable. Cook -up starches such as Colflo 67<sup>tm</sup> are also less preferred, especially for fat continuous base compositions as these will only provide structure after cooking for a considerable amount of time which not compatible with a simple preparation within 3 minutes. Optionally a pre-cooked cook-up starch may be included in a water continuous base composition.

The base composition may comprise citric cell wall material in addition to a cold hydrating viscosifying agent or as an alternative thereto. Examples of suitable material are for example: Herbacel AQ plus citrus fibre<sup>tm</sup> from Herbafood

ingredients GmbH. The citric cell wall material is preferably subjected to a homogenisation treatment before use.

Such material is preferably included in a fat based base composition.

5

Optionally the base composition comprises polysaccharides.

Hydration of polysaccharides in the final product may contribute to a texture which is overall gell-like.

10 In the compositions according to the invention, preferred polysaccharides are high molecular weight polysaccharides such as guar, xanthan, locust bean gum, pecthin, lambda carrageenan, fenugreek, konjac mannan, xyloglucan, carboxymethylcellulose, methylcellulose or a combination thereof.

15 The presence of such a polysaccharide in the base composition is highly preferred because of their effect on droplet size in the final emulsion. It is believed that the presence of a polysaccharide, preferably guar gum, leads to products with smaller average oil droplet size in a final oil in water

20 emulsion. Such products are more stable upon storage and show reduced wetting.

Optionally the base composition comprises a protein. Preferred proteins are milk proteins such as (denatured) whey protein,

25 casein, caseinate or a caseinate replacer, butter milk (powder), skim milk (powder) or a combination thereof.

The base composition can be in any suitable physical form such as a powder, a flowing liquid, a paste, a tablet, a dispersion  
30 of aqueous soluble ingredients in oil. A tablet, powder or aqueous dispersion are most preferred whereas a pourable oil composition or oil slurry such as those disclosed in WO-A-02/00030 are less preferred.

According to a preferred embodiment, the base composition is at least partially transparent. Such composition can for example be a liquid oil comprising dissolved therein oil soluble components of the final emulsion and dispersed therein water soluble components or an aqueous phase comprising dissolved therein (part of the) water soluble components and optionally dispersed oil soluble components of the final emulsion. Preferably the base composition is entirely transparent. Such base composition is suitable for preparing a spreadable water and oil containing composition by adding the remaining ingredients thereto. Such emulsion is generally opaque. The change from at least partially transparent to opaque is an example of a change in sensory properties according to the invention. The R-index for said change was found to be about 100%.

In a further preferred embodiment, the base composition is a powder or a tablet. The transformation of such composition to a water and oil containing emulsion shows a significant change in texture namely from powder or tablet to a plastic emulsion type product. This is an example of the change in sensory properties. Furthermore tablets and powders which are free flowing are easy to handle and their dosing is generally highly reliable.

If the base composition is in the form of a tablet or powder, the consumer may prepare the final spreadable emulsion by the addition of at least water and oil.

Therefore in another aspect the invention relates to a tablet or powder composition suitable for the preparation of an oil in water emulsion said composition comprising a cold hydrating



viscosifying agent or a replacer thereof, a lecithin, caseinate or a caseinate replacer, salt and acidifying agent.

The tablet or powder composition preferably comprises from 35 to 70 weight%, preferably 40 to 65 wt% of a cold hydrating viscosifying agent, from 3 to 30 weight%, preferably from 5 to 25 wt% of a lecithin, from 3 to 30 weight%, preferably from 5 to 25wt% of caseinate or a caseinate replacer, salt, acidifying agent.

- 10 The preferred cold hydrating viscosifying agent is a cold swelling starch. An alternative cold hydrating viscosifying agent is citric cell material as referred to above.

For this tablet or powder, suitable lecithins include for example hydrolysed lecithin such as BOLEC MT<sup>(tm)</sup>, Sterpur E<sup>(tm)</sup>, Adlec E<sup>(tm)</sup>; fractionated lecithin such as the alcohol soluble fraction of native lecithins such as Cetinol<sup>(tm)</sup>, Nathin 3-KE<sup>(tm)</sup>; native lecithin such as Bolec ZT<sup>(tm)</sup>, Adlec<sup>(tm)</sup>, Sterpur PM<sup>(tm)</sup>; and combinations of any of these. Compositions including a  
20 hydrolysed lecithin are highly preferred.

The preferred tablet or powder composition further comprises caseinate or a caseinate replacer. Without wishing to be bound by any theory, it is believed that caseinate plays a dual role  
25 in the final emulsion namely as an emulsifier and as a viscosity enhancer. Optionally caseinate may be replaced with an ingredient or combination of ingredients also fulfilling this function. An example of a suitable caseinate replacer is the combination of an emulsifier such as sorbitan  
30 monopolyoxyethylene (Tween) and a gum such as guar gum.

A preferred tablet or powder composition is composed such that the ratio between the amount of lecithin and the amount of caseinate is from 2:1 to 1:2, preferably from 1.5:1 to 1:1.5.

5 It will be appreciated that the amount and ratio of the ingredients of the tablet or powder will depend on the envisaged ratio of oil and water that is added. It is believed to be within the general capacity of a person skilled in the art to vary the ratio and amount of the individual ingredients  
10 such that a spreadable final emulsion may result.

In an even more preferred embodiment, the tablet or powder composition comprises from 45 to 65 weight% of a cold hydrating viscosifying agent, from 10 to 25 weight% of a  
15 lecithin, from 10 to 25 weight% of caseinate or a caseinate replacer, salt and acidifying agent.

Optionally the tablet or powder composition comprises some oil. It was found that amounts of up to about 10 wt% on total  
20 composition are tolerable. Higher amounts lead to pasty products which are no longer a tablet or a free flowing powder and hence less easy to handle.

Furthermore the tablet or powder composition optionally  
25 comprises a colour composition, flavour composition, preservative or a combination thereof.

In a further aspect the invention relates to the preparation of a tablet said process comprising the steps of mixing lecithin  
30 into powdered components comprising cold hydrating viscosifying agent, caseinate, salt and acidifying agent; compressing the obtained mixture to a tablet.

In an alternative embodiment the base composition is an aqueous composition to which oil and optionally some water is added for preparing a final oil and water containing emulsion. In this  
5 embodiment, the aqueous composition preferably comprises caseinate, a viscosifying agent such as guar, a preservative such as sorbate, and a pre-cooked cook-up starch such as Colflo67<sup>tm</sup>. Such aqueous base composition is preferably pasteurized or sterilized before packaging.

10

In a further alternative embodiment the base composition is a cream. Advantageously such a cream can be used as a cooking product as such e.g. as a cooking cream, a whipping cream or a coffee creamer. Such base composition is turned into a  
15 spreadable product by the addition of a liquid oil, acid, salt and a cold hydrating viscosifying agent. A preferred cold hydrating viscosifying agent in such case is citric cell material which may easily be prepared by a consumer.

The cream preferably comprises from 10 to 40 wt% fat,  
20 preferably from 15 to 35 wt% fat.

Said cream is preferably based on dairy fat, vegetable fat or a combination thereof. Said fat preferably comprises a certain amount of hardstock fat to enable the whippability of the cream. Therefore preferably in this embodiment, at least part  
25 of the fat in the cream is characterised by a solid fat profile of more than 30% solid fat at 5 °C, more than 25% solid fat at 10 °C and more than 25% solid fat at 20 °C.

More preferred at least 50 wt%, even more preferred from 75 to 100 wt% of the total fat or fat blend shows the indicated solid  
30 fat profile.

The solid fat content can be measured by a suitable analytical method such as NMR.

Even more preferred at least 50 wt% of the total fat is solid at 10 °C. Suitable fats in this respect are for example hardened palm kernel oil, coconut fat, hardened coconut fat, 5 (hardened) palm oil, butter fat, fats comprising C14 and/or C16 fatty acids such as laurics, (hardened) babassu oil or mixtures thereof.

Fats comprising a high content of C14 and/or C16 fatty acids are highly preferred as a source of the fat phase, as they tend 10 to show enhanced clumping behaviour and good oral melt properties.

It will be appreciated that a suitable fat blend is preferably of such fat composition that the final product still melts at 15 least partly when consumed.

Especially suitable is a fat blend comprising more than 50% of a partially hardened palm kernel oil, for example a palm kernel oil with a slip melting point of from 35 to 45 °C. 20

Without wishing to be bound by any theory, it is believed that the solid fat present in the base composition of this embodiment, imparts whippability to the product and in the final product promotes the formation of a so called clumped fat 25 phase which is for example disclosed in WO-A-01/10234.

Preferably the cream in this embodiment comprises a protein and an emulsifier.

30 The invention will be illustrated by the following non-limiting examples.

## Examples

### General

#### 5 Determination of G'

Oscillatory shear measurements were performed using a Carrimed CSL500 Rheometer (parallel plate geometry) at a constant temperature of 5°C. (Stress of 10Pa and Frequency of 1Hz). The  
10 sample was loaded onto the rheometer immediately after mixing and values of G' were collected every 30 seconds. The value of G' quoted in Pa is that recorded at a time of 15 minutes after initial shaking.

Stevens value was determined in g by using a Stevens texture  
15 analyser (2 mm/sec, 20 mm depth, mayonnaise grid (mesh 7, thread thickness 0.8 mm, mesh width 2.83 mm,)). Alternatively for harder products a cylindrical probe was used having a diameter of 7 mm with penetration depth of 10 mm.

20 RVA-method to determine suitable cold hydrating viscosifying agents.

### Rapid Visco-Analyser (RVA) - Biopolymer Hydration Test

25 A model emulsion was prepared containing:

|                     |   |
|---------------------|---|
| Sunflower Oil       | 12.5g   |
| Lecithin (Bolec MT) | 2.5g  |
| "test agent"        | 4.0g in case of starch, 1 g in case of a<br>30 gum. |

These ingredients were mixed for 1 minute, at 25 °C, then water 11.25g (equivalent to 45 Parts in 100g formulation) was added.

This mixture was put straight into RVA machine (manufactured by Newport Scientific Pty Ltd) and mixed for 10 mins at 25°C, 180rpm.

- 5 From these data, final viscosity and rate of viscosity development (ie. the maximum gradient between the offset of viscosity increase and the plateau of final viscosity) were derived.

10 Small Deformation Rheology of Instant Spreads

Product was placed on rheometer with parallel plate geometry in oscillation mode, 1mm gap, 4cm diameter.

The experiment consisted of a stress sweep from 1 up to ~1000 Pa.

- 15 The parameters are as follows: frequency 1Hz, temperature 20°C.

From the plot of tan delta vs strain, the value of strain where tan delta = 1 is plotted against the initial tan delta value.

20 Rapid Visco-Analyser (RVA) - Viscosity Development of Instant Spread from Oil paste (example 2-5)

12.5g of Oil paste was stirred until homogeneous for 10 minutes at 25°C. 12.5g of water was added and the two were mixed on the RVA machine (manufactured by Newport Scientific Pty Ltd)

- 25 for 10 mins at 25°C, at a speed of 180rpm.

From these data the increase in viscosity to a maximum plateau value from 0 to 2 minutes was determined.

30 Rapid Visco-Analyser (RVA) - Viscosity Development of Instant Spread from Tablet (Example 1)

2.4g of Tablet was dispersed in 11.9g oil until homogeneous (1 minute at 25°C). 10.7g water as added and the ingredients were

mixed on the RVA machine for 10 minutes at 25°C, at a speed of 180rpm.

From these data the increase in viscosity over 2 to 3 minutes was determined.

5

#### General RVA method

With respect to RVA method for the final emulsion, for different fat/water levels the weights need to be adjusted to give a total amount of 25g product.

10

#### Example 1

A tablet composition with ingredients as listed in table 2 was prepared by mixing Bolec, flavour and colour ingredients into the other, powdered, components of the recipe until a homogeneous dispersion was obtained. The mixture was compressed in a suitable die at a constant 300 psi for approximately 60 seconds.

20 Table 2

| Ingredient   | weight % |
|--|----------|
| Ultratex 4 (starch from National Starch (ICI))           | 43.5     |
| BolecM/T(hydrolysed lecithin from Unimills Zwiijndrecht) | 10.9     |
| Sodium caseinate   | 10.9     |
| Sodium chloride  | 13       |
| Tri sodium citrate                                       | 3.2      |
| Citricacid anhydrous                                     | 1.3      |
| Potassium sorbate  | 1.0      |
| Colour 2% in oil   | 5.4      |
| Flavour in oil   | 10.8     |

The resulting tablet weighed 10 g and was sufficiently strong for handling and packaging and easily crumbled for preparation of an emulsion.

- 5 The emulsion was prepared by mixing the tablet with 50 g of sunflower oil and 45 g water. The mixing was done by manual stirring with a fork for about 2 minutes. Already after this short time a spreadable oil in water emulsion was formed. The R-index of the change in texture from powder to opaque  
10 spreadable emulsion was 100%.

The base composition is suitable for preparing a spread within 2 minutes whereby the consumer shaking the product perceives a change in viscosity of a liquid product to a spreadable  
15 product. The base composition can be sold as such in a pouch or other packaging material.

#### Example 2

20

A paste (the base composition) was prepared comprising the composition according to table 3. The paste was prepared by mixing lecithin in sunflower oil at room temperature, followed by the addition of the other ingredients, like the starch, and  
25 shaking this mixture in a sealed container to disperse the powders in the oil.



Table 3

|   | Base composition        | Final emulsion   |
|---|-------------------------|--|
|   | % of Oil<br>Composition | % wt of total final<br>product weight after<br>mixing with water |
| Sunflower oil                                 | 90.0779                 | 47.3900  |
| sorbitan<br>monopolyoxyethylene<br>(Tween 20) | 0.5322                  | 0.2800   |
| Ultratex 4 <sup>™</sup> ex national<br>starch | 4.5048                  | 2.3700   |
| Sodium Chloride                               | 2.1479                  | 1.1300   |
| Tri-Sodium Citrate                            | 0.5322                  | 0.2800   |
| Citric Acid                                   | 0.2281                  | 0.1200   |
| Potassium Sorbate                             | 0.1711                  | 0.0900   |
| Water   |                         | 47.3900  |
| Guar  | 1.8057                  | 0.9500   |
| Total   | 100.0000                | 100.0000   |

5 To this paste 1 volume equivalent of water was added which corresponds to 47.39 wt% water on final emulsion weight. The resulting product was prepared by shaking the oil phase and the aqueous phase for 2 minutes. The Stevens value of the resulting product was 89 g at 5 °C. The product was spreadable and showed

10 good oral properties. Also the product was stable on storage at 35°C for 14 days.

The base composition is suitable for preparing a spread within 2 minutes whereby the consumer shaking the product perceives a

15 change in viscosity of a liquid product to a spreadable product.

The R-index of the change in texture from oil slurry to opaque spreadable emulsion was 100%.

The base composition can be sold as such in a pouch or other

20 packaging material.

Example 3

A base composition was prepared as in example 2. The composition of the base composition is listed in table 4.

5

Table 4

|   | Base composition        | Final emulsion   |
|---|-------------------------|--|
|   | % wt on oil composition | % wt on total weight of the final emulsion after mixing with water |
| Sunflower oil                               | 88.1057                 | 44.7427  |
| Bolec M/T (hydrolysed lecithin)             | 0.7048                  | 0.3579   |
| Sodium Caseinate                            | 1.1013                  | 0.5593   |
| Ultratex 4 <sup>tm</sup> ex national starch | 5.7269                  | 2.9083   |
| Guar  | 0.8811                  | 0.4474   |
| Hydroxypropylmethylcellulose F4M (HPMC)     | 0.4405                  | 0.2237   |
| Sodium Chloride                             | 2.1145                  | 1.0738   |
| Trisodiumcitrate                            | 0.5286                  | 0.2685   |
| Citric acid                                 | 0.2203                  | 0.1119   |
| Potassium Sorbate                           | 0.1762                  | 0.0895   |
| Water                                       |                         | 49.2170  |
| Total                                       | 100.0000                | 100  |

To this paste 1 volume equivalent of water was added which corresponds to 49.22 wt% water on final emulsion weight. The resulting product was prepared by shaking the oil phase and the aqueous phase for 2 minutes. The Stevens value of the resulting product was 65 g at 5 °C. The product was spreadable and showed good oral properties. Also the product was stable on storage at 35 °C for 14 days.

15

The base composition is suitable for preparing a spread within 2 minutes whereby the consumer shaking the product perceives a change in viscosity of a liquid product to a spreadable product. The R-index of the change in texture from oil slurry to opaque spreadable emulsion was 100%.

20

The base composition can be sold as such in a pouch or other packaging material.

The RVA range for the preparation of the emulsion was from 0 to 5 about 7500cP.

#### Example 4

A base composition was prepared as in example 2. The composition of the base composition is listed in table 5.

10

Table 5

| Ingredient   | Base composition        | Final emulsion after mixing with water |
|--|-------------------------|--|
|  | % wt on oil composition | % wt on total emulsion weight          |
| Sunflower oil  | 91.7431                 | 47.8469                                |
| Manugel <sup>™</sup> (Alginate)                                  | 0.9174                  | 0.4785                                 |
| Manucol <sup>™</sup> Ester M (PGA; polypropylene glycolalginate) | 0.9174                  | 0.4785                                 |
| Calcium Carbonate  | 0.1835                  | 0.0957                                 |
| Tri-Sodium Citrate   | 0.2752                  | 0.1435                                 |
| Citric Acid  | 0.2752                  | 0.1435                                 |
| NaCl   | 1.8349                  | 0.9569                                 |
| Potassium Sorbate  | 0.1835                  | 0.0957                                 |
| Ultratex 4 <sup>™</sup> ex national starch                       | 3.6697                  | 1.9139                                 |
| Water  |                         | 47.8469                                |
|  | 100.0000                | 100.0000                               |

To this paste 1 volume equivalent of water was added which corresponds to 47.85 wt% water on final emulsion weight. The resulting product was prepared by shaking the oil phase and the aqueous phase for maximum 2 minutes. The R-index of the change in texture from oil slurry to opaque spreadable emulsion was 100%. After the emulsion had been left to stand for 10 minutes, it was stirred. The Stevens value of the resulting product was about 50 g at 5 °C. The product was spreadable and showed good

oral properties. Also the product was stable on storage at 35 °C for 14 days.

The base composition is suitable for preparing a spread within 2 minutes whereby the consumer shaking the product perceives a change in viscosity of a liquid product to a spreadable product.

The base composition can be sold as such in a pouch or other packaging material.

#### 10 Example 5

A base composition was prepared as in example 2. The composition of the base composition is listed in table 6.

15 Table 6

|   | Base composition        | Final emulsion after mixing with water     |
|---|-------------------------|--|
|   | % wt on oil composition | % wt on total weight of the final emulsion |
| Sunflower oil                               | 90.7935                 | 47.5873                                    |
| Low methoxy Pectin (LM12 CG-Z)              | 1.8159                  | 0.9517                                     |
| Beet-Pectin                                 | 0.9079                  | 0.4759                                     |
| Calcium Carbonate                           | 0.3632                  | 0.1903                                     |
| Tri-Sodium Citrate                          | 0.2724                  | 0.1428                                     |
| Citric Acid                                 | 0.2179                  | 0.1142                                     |
| Sodium Chloride                             | 1.8159                  | 0.9517                                     |
| Potassium Sorbate                           | 0.1816                  | 0.0952                                     |
| Ultratex 4 <sup>tm</sup> ex national starch | 3.6317                  | 1.9035                                     |
| Water                                       |                         | 47.5873                                    |
|   | 100.0000                | 100.0000                                   |

To this paste 1 volume equivalent of water was added which corresponds to 47.59 wt% water on final emulsion weight. The resulting product was prepared by shaking the oil phase and the aqueous phase for 2 minutes. The base composition is suitable for preparing a spread within 2 minutes whereby the consumer

shaking the product perceives a change in viscosity of a liquid product to a spreadable product. The R-index of the change in texture from oil slurry to opaque spreadable emulsion was 100%. The emulsion was left to stand for 10 minutes and then stirred.

5 The Stevens value of the resulting product was about 55 g at 5 °C. The product was spreadable and showed good oral properties. Also the product was stable on storage at 35 °C for 14 days. The base composition can be sold as such in a pouch or other packaging material.

**Claims**

1. Method for the preparation of a spreadable oil and water comprising emulsion, comprising mixing a base composition with oil and/or water by a simple, preferably manual operation, characterised in that the spreadable emulsion is prepared within 3 minutes and the preparation is accompanied by a change in sensory properties which is demonstrated by an R-index in the R-index sensitivity test of more than 80%.
2. Method according to claim 1 wherein the spreadable emulsion is prepared within 2 minutes.
3. Method according to claim 1 or claim 2 wherein the change in sensory properties is a change in flavour, texture, colour, aroma or a combination thereof.
4. Method according to any of claims 1-3 wherein the change in sensory properties is demonstrated by an R-index in the R-index sensitivity test of more than 90%.
5. Method according to any of claims 1-4 wherein the change in sensory properties is a change in texture.
6. Method according to any of claims 1-5 wherein the base composition is at least partially transparent.
7. Method according to any of claims 1-6 wherein the emulsion is an oil in water emulsion.

8. Base composition for use in a method according to any of claims 1-7, characterised in that said base composition is a powder or a tablet.
9. Tablet or powder composition suitable for preparing an oil in water emulsion, said composition comprising a cold hydrating viscosifying agent, a lecithin, caseinate or a caseinate replacer, salt and acidifying agent.
10. Tablet or powder composition according to claim 9 wherein the composition comprises from 35 to 70 weight% of a cold hydrating viscosifying agent, from 3 to 30 weight% of a lecithin, from 3 to 30 weight% of caseinate or a caseinate replacer, salt and acidifying agent.
11. Tablet or powder composition according to claim 10 wherein ratio between the amount of lecithin and the amount of caseinate is from 2:1 to 1:2, preferably from 1.5:1 to 1:1.5.
12. Process for the preparation of a tablet according to any of claims 9-11 said process comprising the steps of mixing lecithin into powdered components comprising cold hydrating viscosifying agent, caseinate, salt and acidifying agent; compressing the obtained mixture to a tablet.
13. Use of a base composition according to claim 8 or a tablet or powder according to any of claims 9-11 for the preparation of an oil in water emulsion.

# INTERNATIONAL SEARCH REPORT

Internu I Application No  
PCT/EP 02/13310

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>IPC 7 A23D7/00 A23D7/04 A23L1/035 A23L1/0522 A23P1/06<br>A23P1/02   |   |  |
|---|---|--|
| According to International Patent Classification (IPC) or to both national classification and IPC   |   |  |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>IPC 7 A23D A23L A23P  |   |  |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched   |   |  |
| Electronic data base consulted during the International search (name of data base and, where practical, search terms used)<br>EPO-Internal, WPI Data, PAJ, FSTA, BIOSIS   |   |  |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>   |   |  |
| Category *  | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.  |
| X   | DATABASE WPI<br>Section Ch, Week 199836<br>Derwent Publications Ltd., London, GB;<br>Class A97, AN 1998-425728<br>XP002199424<br>& RU 2 101 981 C (TARASOVA L I),<br>20 January 1998 (1998-01-20)<br>abstract | 8-11,13  |
| X   | EP 0 796 567 A (NESTLE SA)<br>24 September 1997 (1997-09-24)<br>cited in the application<br>column 2, line 5-9,31-44<br>column 3, line 51-56<br>column 4, line 14-17<br>claim 1; example 1                    | 1-13   |
| -/-   |   |  |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.   |   |  |
| * Special categories of cited documents :<br>*A* document defining the general state of the art which is not considered to be of particular relevance<br>*E* earlier document but published on or after the international filing date<br>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>*O* document referring to an oral disclosure, use, exhibition or other means<br>*P* document published prior to the international filing date but later than the priority date claimed<br>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<br>*Z* document member of the same patent family |   |  |
| Date of the actual completion of the international search<br><br>13 May 2003  |   | Date of mailing of the international search report<br><br>22/05/2003 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+31-70) 340-3016   |   | Authorized officer<br><br>Rooney, -K                                 |



# INTERNATIONAL SEARCH REPORT

Intern: Application No

PCT/EP 02/13310

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT |  |                       |
|--|--|-----------------------|
| Category *   | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
| X  | EP 0 821 885 A (RAFFINERIE TIRLEMONTAISE SA) 4 February 1998 (1998-02-04)<br>examples 1,2,4<br>----  | 8-11,13               |
| X  | US 5 658 609 A (ABBOUD AMNA ET AL)<br>19 August 1997 (1997-08-19)<br>examples 9,10<br>----   | 8-11                  |
| X  | DATABASE WPI<br>Section Ch, Week 198044<br>Derwent Publications Ltd., London, GB;<br>Class D13, AN 1980-77967C<br>XP002240093<br>& JP 55 120746 A (RIKEN VITAMIN OIL CO LTD), 17 September 1980 (1980-09-17)<br>abstract<br>---- | 8-11                  |
| A  | US 4 933 192 A (DARLING DONALD F ET AL)<br>12 June 1990 (1990-06-12)<br>See whole document<br>-----  | 1-13                  |

# INTERNATIONAL SEARCH REPORT

nation on patent family members

Interr al Application No  
PC1/EP 02/13310

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---|---------------------|----------------------------|---------------------|
| RU 2101981                                | C | 20-01-1998          | RU 2101981 C1              | 20-01-1998          |
| EP 0796567                                | A | 24-09-1997          | EP 0796567 A1              | 24-09-1997          |
|   |   |                     | AT 207311 T                | 15-11-2001          |
|   |   |                     | AU 725219 B2               | 05-10-2000          |
|   |   |                     | AU 1253997 A               | 14-08-1997          |
|   |   |                     | AU 717986 B2               | 06-04-2000          |
|   |   |                     | AU 1601697 A               | 28-08-1997          |
|   |   |                     | CA 2196910 A1              | 08-08-1997          |
|   |   |                     | CA 2244233 A1              | 14-08-1997          |
|   |   |                     | CN 1210447 A ,B            | 10-03-1999          |
|   |   |                     | CZ 9700333 A3              | 15-10-1997          |
|   |   |                     | CZ 9802483 A3              | 16-12-1998          |
|   |   |                     | DE 69707649 D1             | 29-11-2001          |
|   |   |                     | DE 69707649 T2             | 08-05-2002          |
|   |   |                     | EG 20646 A                 | 31-10-1999          |
|   |   |                     | WO 9728705 A1              | 14-08-1997          |
|   |   |                     | EP 0787437 A2              | 06-08-1997          |
|   |   |                     | EP 0884956 A1              | 23-12-1998          |
|   |   |                     | HU 9700365 A2              | 28-01-1998          |
|   |   |                     | JP 9215486 A               | 19-08-1997          |
|   |   |                     | JP 2000505287 T            | 09-05-2000          |
|   |   |                     | NO 970384 A                | 08-08-1997          |
|   |   |                     | NZ 314191 A                | 25-02-1999          |
|   |   |                     | NZ 331181 A                | 28-01-2000          |
|   |   |                     | PL 318344 A1               | 18-08-1997          |
|   |   |                     | PL 328195 A1               | 18-01-1999          |
|   |   |                     | RU 2177694 C2              | 10-01-2002          |
|   |   |                     | RU 2149571 C1              | 27-05-2000          |
|   |   |                     | SK 15997 A3                | 10-09-1997          |
|   |   |                     | SK 105598 A3               | 02-12-1998          |
|   |   |                     | TR 9700088 A2              | 21-08-1997          |
|   |   |                     | TR 9801502 T2              | 21-10-1998          |
|   |   |                     | TW 419356 B                | 21-01-2001          |
|   |   |                     | US 6214406 B1              | 10-04-2001          |
|   |   |                     | US 5916612 A               | 29-06-1999          |
|   |   |                     | ZA 9700871 A               | 03-08-1998          |
| EP 0821885                                | A | 04-02-1998          | EP 0821885 A1              | 04-02-1998          |
|   |   |                     | AU 727609 B2               | 14-12-2000          |
|   |   |                     | AU 2871897 A               | 05-02-1998          |
|   |   |                     | BR 9707104 A               | 12-09-2000          |
|   |   |                     | CA 2211926 A1              | 31-01-1998          |
|   |   |                     | DE 69624805 D1             | 19-12-2002          |
|   |   |                     | DK 821885 T3               | 10-03-2003          |
|   |   |                     | JP 10179025 A              | 07-07-1998          |
|   |   |                     | NZ 328405 A                | 28-10-1998          |
|   |   |                     | PL 321416 A1               | 02-02-1998          |
| US 5658609                                | A | 19-08-1997          | US 5939127 A               | 17-08-1999          |
|   |   |                     | US 5851576 A               | 22-12-1998          |
|   |   |                     | CA 2150515 A1              | 30-12-1995          |
| JP 55120746                               | A | 17-09-1980          | JP 1403193 C               | 28-09-1987          |
|   |   |                     | JP 58011833 B              | 04-03-1983          |
| US 4933192                                | A | 12-06-1990          | AT 76562 T                 | 15-06-1992          |
|   |   |                     | AU 590694 B2               | 09-11-1989          |

# INTERNATIONAL SEARCH REPORT

nation on patent family members

Intern # Application No

PCT/EP 02/13310

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---------------------|----------------------------|---------------------|
| US 4933192                                | A                   | AU 7052287 A               | 01-10-1987          |
|   |                     | CA 1297722 A1              | 24-03-1992          |
|   |                     | DE 3779348 D1              | 02-07-1992          |
|   |                     | EP 0239378 A2              | 30-09-1987          |
|   |                     | JP 62253338 A              | 05-11-1987          |
|   |                     | ZA 8702273 A               | 30-11-1988          |
| <hr/>                                     |                     |                            |                     |